Correlation between Continuous/Discontinuous Yielding and Hall–Petch Slope in High Purity Iron

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High purity iron specimens containing 11 ppm carbon and 8 ppm nitrogen with different grain sizes were fabricated by cold rolling and subsequent annealing. It was found that the specimens exhibited entirely different yielding behavior in tensile tests depending on different cooling processes after annealing. The water-cooled specimens exhibited continuous yielding while the air-cooled ones exhibited discontinuous yielding. It was found that the Hall–Petch slope, $k_y$, significantly changed depending on the different yielding behaviors.

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1. Introduction

The yield stress increases with decreasing the mean grain size in polycrystalline metallic materials, according to well-known Hall–Petch relationship:1,2)

$$\sigma_y = \sigma_0 + k_y d^{-1/2}$$  \hspace{1cm} (1)

where $\sigma_y$ is yield stress, $\sigma_0$ friction stress, $k_y$ Hall–Petch slope, and $d$ mean grain size. Different models have been proposed to explain the Hall–Petch relationship,2,4) but its precise physical meaning remains still unclear. Based on the most frequently used pile-up model,2,3) the term $k_y$ is usually considered as the ability of grain boundary to resist the plastic deformation transmission from one grain to its neighbors.

It has been believed that the $k_y$ for commercial purity iron and low carbon steels is constant around 600 MPa·µm$^{1/2}$.5) On the other hand, recently Takeda et al.6,7) revealed that the $k_y$ significantly decreased with decreasing the carbon content from 56 to 4 mass ppm in pure irons. Furthermore, it has been found that the $k_y$ of ultra-low carbon interstitial free (IF) steels, in which solute interstitial atoms (C and N) are scavenged by Ti and Nb through forming carbides and nitrides, is very small around 120 MPa·µm$^{1/2}$.8,9) IF steels exhibit continuous yielding behavior during tensile test, although it is well-known that commercial-purity iron and low carbon steels usually show discontinuous yielding behavior characterized by distinct yield-drop and Lüders deformation.

On the other hand, recent research revealed much higher $k_y$ values in ultra-fine grained (UFG) aluminum and IF steels compared with their conventional grain sized counterparts.8,10,11) Discontinuous yielding was unexpectedly found in those UFG materials while their conventional grain sized counterparts exhibit continuous yielding as is well-known. Above results suggest certain dependence between yielding behaviors and Hall–Petch relationship, but studies about this point have been rarely carried out.

The aim of the present study is to confirm whether the yielding behaviors and Hall–Petch relationship have some correlations or not. In this paper we demonstrate a clear dependence between yielding behavior and Hall–Petch slope in a high-purity iron. We have found different yielding behaviors occurred in an identical high-purity iron, depending on the heat treatment. The Hall–Petch slope, $k_y$, was significantly higher in the specimens showing discontinuous yielding than that in the specimens showing continuous yielding.

2. Experiments

A high purity iron containing 11 ppm carbon and 8 ppm nitrogen was used in the present study. The chemical composition of the material is shown in Table 1. Starting plates with different thicknesses were subjected to 50–90% cold rolling to obtain sheets having a constant thickness of 1 mm. The cold-rolled sheets were then annealed in a vacuum furnace at various temperatures ranging from 723 to 873 K for 1.8 ks in order to achieve various mean grain sizes. The specimens were either water-cooled (WC) or air-cooled (AC) to room temperature after annealing. Microstructures of the specimens were observed on longitudinal sections perpendicular to the transverse direction (TD) of the sheets by optical microscopy and electron back-scattering diffraction (EBSD) system in a scanning electron microscope (SEM) equipped with field-emission type gun. The processes and obtained grain sizes of the specimens are summarized in Table 2. Only the specimens having fully recrystallized microstructures were provided to subsequent tensile tests in the present study. Mechanical properties of the specimens were investigated by an uniaxial tensile test at room temperature at an initial strain rate of $8.3 \times 10^{-4}$ s$^{-1}$. The tensile test specimens with 10 mm in gauge length and 5 mm in gauge width were used, which had 1/5 miniature size of the JIS-5 standard specimen. An extensometer was attached on the specimens in the tensile test to measure the precise displacement.

Table 1 Chemical composition of the high purity iron used in this study (mass ppm).

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Al</th>
<th>O</th>
<th>Ti</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>11</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>&lt;20</td>
<td>&lt;20</td>
<td>300</td>
<td>14</td>
<td>&lt;20</td>
<td>8</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

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According to the well-known theory of Cottrell and Bilby,12) yielding behaviors could be realized in the same material. It should be noted that different types of cooled specimens exhibited discontinuous yielding characteristics, while the air-cooled specimens exhibited continuous yielding, with the water-cooled specimens not giving considerable effect on the grain size. Table 2, indicating that air-cooling or water-cooling process during cold-rolling and annealing had a significant effect on the grain size heterogeneity and texture of the present specimens.

Table 2 Deformation and annealing conditions of the pure iron specimens together with the mean grain sizes. WC and AC mean water-cooling and air-cooling, respectively. Only the specimens having fully recrystallized microstructures are summarized in the table.

<table>
<thead>
<tr>
<th>Cold-Rolling reduction</th>
<th>Annealing condition</th>
<th>Mean grain size</th>
<th>Cold-Rolling reduction</th>
<th>Annealing condition</th>
<th>Mean grain size</th>
</tr>
</thead>
<tbody>
<tr>
<td>90%</td>
<td>650°C#1.8 ks+WC</td>
<td>15.2 µm</td>
<td>90%</td>
<td>650°C#1.8 ks+AC</td>
<td>13.6 µm</td>
</tr>
<tr>
<td></td>
<td>700°C#1.8 ks+WC</td>
<td>16.2 µm</td>
<td></td>
<td>700°C#1.8 ks+AC</td>
<td>13.8 µm</td>
</tr>
<tr>
<td></td>
<td>750°C#1.8 ks+WC</td>
<td>17.5 µm</td>
<td></td>
<td>750°C#1.8 ks+AC</td>
<td>17.4 µm</td>
</tr>
<tr>
<td>85%</td>
<td>700°C#1.8 ks+WC</td>
<td>17.3 µm</td>
<td>85%</td>
<td>700°C#1.8 ks+AC</td>
<td>16.9 µm</td>
</tr>
<tr>
<td></td>
<td>750°C#1.8 ks+WC</td>
<td>21.8 µm</td>
<td></td>
<td>750°C#1.8 ks+AC</td>
<td>22.8 µm</td>
</tr>
<tr>
<td>75%</td>
<td>700°C#1.8 ks+WC</td>
<td>25.4 µm</td>
<td>75%</td>
<td>700°C#1.8 ks+AC</td>
<td>23.5 µm</td>
</tr>
<tr>
<td></td>
<td>750°C#1.8 ks+WC</td>
<td>27.7 µm</td>
<td></td>
<td>750°C#1.8 ks+AC</td>
<td>29.3 µm</td>
</tr>
<tr>
<td></td>
<td>800°C#1.8 ks+WC</td>
<td>36.7 µm</td>
<td></td>
<td>800°C#1.8 ks+AC</td>
<td>38.4 µm</td>
</tr>
<tr>
<td>50%</td>
<td>750°C#1.8 ks+WC</td>
<td>45.1 µm</td>
<td>50%</td>
<td>750°C#1.8 ks+AC</td>
<td>41.8 µm</td>
</tr>
</tbody>
</table>

3. Results and Discussion

Grain boundary maps obtained from EBSD measurement of two specimens displaying typical fully recrystallized microstructures after annealing are shown in Fig. 1. The grains are nearly equiaxed and the mean grain sizes of the specimens are 13.6 and 45.1 µm, respectively. The mean grain sizes were measured by mean interception method. The black and gray lines in Fig. 1 indicate high-angle grain boundaries having misorientation larger than 15° and low-angle grain boundaries with misorientation ranging from 2 to 15°, respectively. The boundaries having misorientation smaller than 2° were removed in order to remove the inaccuracy in EBSD measurement and analysis. The equiaxed grains in Fig. 1 are mostly surrounded by high-angle grain boundaries. Although some heterogeneities in grain size were observed in the 50% cold-rolled and annealed specimens (like Fig. 1(b)), the grain size distributions did not show any bimodal ones but monomodal distributions were found. That is, the grain size heterogeneity is not so significant even in the specimen cold-rolled by the lowest rolling reduction (50%). The specimens used in the present study had typical {111}uvw (as major component) plus [001]110 (as minor component) textures, but the textures were not sharp even in the 90% cold-rolled and annealed specimens. Therefore, the authors think that the heterogeneity and texture of the present specimens do not significantly affect the Hall–Petch relationship described later. It is noteworthy that similar mean grain sizes could be obtained by identical combination of cold rolling reduction and annealing temperature as shown in Table 2, indicating that air-cooling or water-cooling process did not give considerable effect on the grain size.

Figures 2(a) and 2(b) display typical nominal stress–strain curves selected from the water-cooled and air-cooled specimens, respectively. It is very interesting that the water-cooled specimens exhibited continuous yielding, while the air-cooled specimens exhibited discontinuous yielding characterized by distinct yield-drop and subsequent Lüders deformation. It should be noted that different types of yielding behaviors could be realized in the same material. According to the well-known theory of Cottrell and Bilby,12) the occurrence of discontinuous yielding in the present material is considered to be attributed to the mechanism based on the lack of mobile dislocations locked-in by interstitial carbon and nitrogen atoms. During air-cooling, carbon and nitrogen atoms have enough time to form atmosphere around dislocations or/and dislocation sources. In the water-cooled specimens exhibiting continuous yielding the interstitial atoms rarely segregate on mobile dislocations due to rapid cooling from annealing temperature. Compared with the previous studies on low carbon steels and IF steels,7–9) the present results suggest that yielding behaviors are affected not only by the total content of the interstitial elements in the material but also the distribution of the interstitials controlled by heat treatments.

In order to conduct a Hall–Petch analysis, 0.2% offset proof stress (σ0.2%) was taken as the yield strength for the WC specimens exhibiting continuous yielding. For the AC specimens exhibiting discontinuous yielding, upper yield stress (σUY) and lower yield stress (σLY) were used. In addition, we carried out an extrapolation process on the true
stress–strain curves to obtain $\sigma_{0.2\%}$ even from the discontinuous yielding curves.\textsuperscript{13)} The extrapolation technique was conducted using the Hollomon equation:

$$\sigma = K\varepsilon^n$$

where $\sigma$ is the flow stress, $K$ is strength index, $\varepsilon$ is the true strain and $n$ is strain hardening exponent. The extrapolation process on an air-cooled specimen was illustrated in Fig. 3(a). The work hardening region of the true stress–strain curve was fitted with Hollomon equation and extrapolated back to the elastic deformation region. The fitted and extrapolated curves exhibit continuous yielding, from which the $\sigma_{0.2\%}$ could be determined even from discontinuous yielding curves. The extrapolation technique was also carried out for the water-cooled specimens and the $\sigma_{0.2\%}$ was measured from the extrapolated curves, as shown in Fig. 3(b). It should be noted that although the water-cooled specimens exhibited continuous yielding, the transition from elastic deformation to plastic deformation was still somehow discontinuous, compared with the extrapolated stress–strain curve with a perfectly continuous yielding character. We consider that weak Cottrell atmosphere by interstitial atoms is formed even during water-cooling or at annealing temperature. As a result, the mobile dislocations (or dislocation sources) are locked by the weak Cottrell atmosphere and the water-cooled specimens exhibit slightly abrupt yielding behaviors instead of perfectly continuous yielding.

The $\sigma_{UYS}$ and $\sigma_{LY}$ of the AC specimens, and the $\sigma_{0.2\%}$ of the WC specimens, as well as the $\sigma_{0.2\%}$ obtained from the extrapolated curves are plotted against $d^{-1/2}$ in Fig. 4(a) and 4(b). Then the Hall–Petch relationship for each case was obtained by least square fitting method. The results show that $\sigma_{0.2\%}$ of the WC specimens and $\sigma_{UYS}$, $\sigma_{LY}$ of the AC specimens all increase linearly with increasing the $d^{-1/2}$ obeying Hall–Petch relationship ($\sigma_{0.2\%} = 71 + 168d^{-1/2}$, $\sigma_{UYS} = 12 + 650d^{-1/2}$, $\sigma_{LY} = 32 + 456d^{-1/2}$). However, the $k_y$ (168 MPa·µm$^{-1/2}$) evaluated from the $\sigma_{0.2\%}$ of the WC specimens which exhibited continuous yielding, is much lower than those (650 MPa·µm$^{-1/2}$, 456 MPa·µm$^{-1/2}$) obtained from the $\sigma_{UYS}$ and $\sigma_{LY}$ of the AC specimens which exhibited discontinuous yielding. In other words, discontinuous yielding greatly enhances the Hall–Petch slope, indicating that different yielding behavior has a significant effect on the Hall–Petch slope, even in the same material. Interestingly, the $\sigma_{0.2\%}$ measured from the extrapolated curves of the WC and AC specimens had a nearly identical relationship ($\sigma_{0.2\%} = 52 + 127d^{-1/2}$, $\sigma_{0.2\%} = 39 + 170d^{-1/2}$). The Hall–Petch relationships obtained from the AC, WC specimens and their extrapolated curves are gathered in Fig. 4(c). The Hall–Petch relationship of an IF steel ($\sigma_{0.2\%} = 54 + 112d^{-1/2}$) given by Kamikawa\textsuperscript{14)} is also included for comparison. An obvious dependence of the Hall–Petch slope on yielding behaviors can be observed. The $k_y$ values obtained from continuous yielding are very similar to each other and much lower than those obtained from discontinuous yielding. It implies that an intrinsic and extremely low $k_y$ between 100–200 MPa·µm$^{-1/2}$ exists in pure iron, which is not affected by discontinuous yielding. This extremely low $k_y$ might be related to the essential ability of grain boundary to resist plastic deformation transmission in the material.

As was mentioned in the introduction, Takeda et al.\textsuperscript{6)} found that the $k_y$ significantly decreased with decreasing the carbon content in pure iron. They thought that this was because grain boundary ledges were suppressed to act as dislocation sources by grain boundary segregation of carbon, based on the grain boundary ledge mechanism for explaining Hall–Petch relationship by Li,\textsuperscript{9)} although no evidence of grain boundary segregation and no evidence supporting that the grain boundary ledges were the main dislocation sources in the materials were shown.\textsuperscript{15)} Takahashi et al.\textsuperscript{7)} carried out 3-dimensional atom-probe analysis of the pure irons used in Ref. 6) and confirmed segregation of carbon and nitrogen atoms at grain boundaries. They also discussed a significant

![Fig. 2](image)

![Fig. 3](image)
The difference between carbon and nitrogen in the effects on Hall–Petch slope (if the grain boundary segregation really controlled $k_y$), but the reason of the difference was unclear.\textsuperscript{6,7} According to the grain boundary ledge model, if the carbon content is constant in the material, a decrease in $k_y$ is expected by grain refinement because the density of carbon on the grain boundary decreases with increasing the grain boundary area per unit volume (i.e., with decreasing the mean grain size). Such a decreasing in $k_y$ by grain refinement (in the range of several hundred nm to several µm) has not been found in any previous experiments, but an extra hardening has rather been reported in ultra-fine grained materials.\textsuperscript{10,14} Furthermore, if the grain boundary ledges are the main dislocation sources and the discontinuous yielding in the present study is caused by the carbon segregation on the grain boundary, the discontinuous yielding is expected to be less prominent when the mean grain size decreases. However, the actual results are opposite in the present study (Fig. 2). It is known also by the previous studies\textsuperscript{8,15} that the grain refinement enhances yield-point phenomena. It can be, therefore, concluded that there is no reason to stick to the grain boundary segregation of interstitial atoms for explaining the change in the $k_y$. We believe that the change in $k_y$ is attributed to the change in the yielding behaviors, as is clearly shown in the present study. Takeda et al.\textsuperscript{10} did not show any stress–strain data including the yielding behaviors of their materials.

4. Conclusion

The present study demonstrated that an identical high-purity iron exhibited different yielding behaviors, i.e., discontinuous yielding and continuous yielding. The Hall–Petch slope, $k_y$, showed a clear dependence on the yielding behaviors. Discontinuous yielding resulted a much higher $k_y$ than continuous yielding. By the extrapolation process on the true stress–strain curve, the effect of discontinuous yielding on $k_y$ was eliminated and extremely low $k_y$ value between 100–200 MPa·µm$^{1/2}$ was found in the high-purity iron. We believe that the present study provides an important aspect of the Hall–Petch relationship from a viewpoint of yielding behavior, which could throw light on the essential meaning of the Hall–Petch slope in future.

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REFERENCES